

PATENT COOPERATION TREATY

PCT


INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 25 JAN 2007

WIPO PCT

Applicant's or agent's file reference 11321P077WO	FOR FURTHER ACTION See Form PCT/PEA/416	
International application No. PCT/US2004/034002	International filing date (day/month/year) 14.10.2004	Priority date (day/month/year) 14.10.2003
International Patent Classification (IPC) or national classification and IPC INV. C01B31/02 C01B3/00		
Applicant WILLIAM MARSH RICE UNIVERSITY		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 10 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> sent to the applicant and to the International Bureau) a total of sheets, as follows:</p> <p style="margin-left: 40px;"><input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p style="margin-left: 40px;"><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input checked="" type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input checked="" type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input checked="" type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input checked="" type="checkbox"/> Box No. VIII Certain observations on the international application</p>		
Date of submission of the demand 10.05.2005	Date of completion of this report 17.01.2007	
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer CORRIAS, M Telephone No. +31 70 340-	



**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/US2004/034002

Box No. I Basis of the report

1. With regard to the **language**, this report is based on
- ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
 - ☐ international search (under Rules 12.3(a) and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4(a))
 - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a))
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1-24 as originally filed

Claims, Numbers

1-78 as originally filed

Drawings, Figures

1-8 as originally filed

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/US2004/034002

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

- ☐ the entire international application,
☒ claims Nos. 68-75

because:

- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):
- ☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):
- ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed (*specify*).
- ☒ no international search report has been established for the said claims Nos. 68-75
- ☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:
- ☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Preliminary Examining Authority in a form and manner acceptable to it.
- ☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Preliminary Examining Authority in a form and manner acceptable to it.
- ☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rules 13*ter*.1(a) or (b) and 13*ter*.2.
- ☐ a meaningful opinion could not be formed without the tables related to the sequence listings; the applicant did not, within the prescribed time limit, furnish such tables in electronic form complying with the technical requirements provided for in Annex C-*bis* of the Administrative Instructions, and such tables were not available to the International Preliminary Examining Authority in a form and manner acceptable to it.
- ☐ the tables related to the nucleotide and/or amino acid sequence listing, if in electronic form only, do not comply with the technical requirements provided for in Annex C-*bis* of the Administrative Instructions.
- ☐ See separate sheet for further details

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/US2004/034002

Box No. IV Lack of unity of invention

1. ☐ In response to the invitation to restrict or pay additional fees, the applicant has, within the applicable time limit:
- ☐ restricted the claims.
 - ☐ paid additional fees.
 - ☐ paid additional fees under protest and, where applicable, the protest fee.
 - ☐ paid additional fees under protest but the applicable protest fee was not paid.
 - ☐ neither restricted the claims nor paid additional fees.
2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is:
- ☐ complied with.
 - ☒ not complied with for the following reasons:
see separate sheet
4. Consequently, this report has been established in respect of the following parts of the international application:
- ☐ all parts.
 - ☒ the parts relating to claims Nos. 1-67 and 76 -78 .

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/US2004/034002

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	5, 7-9, 11-12, 14-16, 20-21,26-27,30,32-33,37-38,45-46,51,53-55,57-58,61,63
	No: Claims	1- 4,6, 10,13, 17-19, 22-25, 28-29,31,34-36,39-44,47-50,52,56,59-60,62,64-67,76-78
Inventive step (IS)	Yes: Claims	11-12,14-16,32-33,45,51,57-58
	No: Claims	1-10,13,17-31,34-44,46-50,52-56,59-67,76-78
Industrial applicability (IA)	Yes: Claims	1-67,76-78
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VI Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Reference is made to the following documents:

D1: US2002/0004028

D2: XP002325910

D3: XP002977463

D4: WO2003084869

Re Item IV

Lack of unity of invention

1.1 This Authority considers that there are 2 inventions covered by the claims indicated as follows:

Invention I: Claims 1-67 and 76-78 directed to processes to amplify carbon nanotubes of a specific type by a seed growth, and to the preparation of the SWNT-metal cluster that act seeds.

Invention II: Claims 68-75 directed to the synthesis of the metal cluster FeMoC.

1.2 The inventions are not so linked as to form a single general inventive concept, as required by Rule 13.1 PCT for the following reason: the product of invention II (claims 68 to 73) is a metallic compound and has a totally different nature when compared to the ones present in invention I (claims 39, 57 and 58) which deal with modified carbon nanotubes. However, it is claimed (claims 74 and 75) that the metal cluster FeMoC obtained as in claims 68 to 73 can be used as a catalyst precursor in the process of obtaining SWNT-metal clusters suitable for a seed growth method. Thus, the general linking concept between inventions I and II is the modification of carbon nanotubes with metal compounds.

1.3 The preparation of complexes obtained by the reaction of functionalised carbon nanotubes and metal compounds which can be further transformed to metal clusters by reductive heating is already disclosed in document D1 (see paragraphs 152 to 201). Thus, the general concept linking inventions I and II is not novel.

1.4 Due to the reason set forth in 1.3 the requirements of Rule 13.1 PCT are not met. The searching authority has performed a partial search which relates to the invention I mentioned above. The applicant is invited to pay an additional search fee for the invention

II as stated above.

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1) Novelty

1.1 The document D1 discloses (see paragraphs 56 to 63 and 152 to 201) a process to achieve amplification of preselected carbon nanotubes which have undergone different steps: cutting single walled nanotubes (see paragraph 169), sorting them by geometry but taking into account the chirality (see paragraphs 156 and 169), docking on them a catalyst metal cluster precursor which can be activated by heating in a reductive atmosphere (e.g. in the presence of hydrogen) (see paragraphs 178 to 180 and 193 to 197) to and further growing SWNT by elongating the seed molecule by several orders of magnitude (see paragraphs 163 and 198 to 200).

1.2 Furthermore, document D1 discloses that sidewall derivatization can be performed on the starting SWNT seeds (see paragraph 194), and that prior to the elongation step they can be deposited on a support (see paragraphs 196 and 197), it is also said that the seeds can be obtained from the product of an initial seed-growth step (see paragraph 195).

1.3 Document D1 also discloses the chemical modification of carbon nanotubes. In particular SWNT sidewalls and open ends can be derivatized with fluorine (see paragraphs 85 to 96) and can further be reacted with other functionalities (e.g. metal precursors) to obtain chemically modified SWNT which can be easily solvated and separated (see paragraph 100) and can lead to the formation of SWNT-metal complexes by the use of linking agents (see paragraphs 64 to 81). Particular examples of metals suitable to be docked on the functionalized nanotubes are group VI b or VII b metals (see paragraph 69).

1.4 Therefore the subject-matter of claims 1 to 4, 6, 10, 13, 17 to 19, 22 to 25, 28, 29, 31, 34 to 36, 39 to 44, 47-50, 52, 56, 59, 60, 62, 64 to 67 and 76 to 78 is not novel and does not meet the requirements of Article 33 (2) PCT.

2) Inventive step

2.1 Dependent claims 5, 20, 21, 30, 37 and 38 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step (Article 33 (3) PCT), the reasons being as follows: the claimed processes used to cut nanotubes, the use of aerosols in the growth phase and the gaseous mixture comprising CO and hydrogen are common in the field of carbon nanotubes and the person skilled would have thought of using them without the exercise of inventive skill.

2.2 Document D1 is considered to be the closest prior art to the subject-matter of claims 7 to 9 and discloses (see paragraphs 156 to 163) that growth of a specific type of nanotubes can be achieved by a seed-growth method on selected starting SWNT. The subject-matter of claims 7-9 therefore differs from this known D1 in that a specific method of sorting is disclosed. The remaining problem to be solved is therefore regarded as how to provide an alternative method. The use of selective chemical derivatization based on type in order to separate semiconducting and metallic SWNT is described in document D2 (see pages 1519 and 1520) as providing the same advantages as in the present application. The skilled person would therefore regard it as a normal option to include this feature in the process described in document D1 in order to solve the problem posed. Thus, the subject-matter of claims 7 to 9 does not meet the requirements of Article 33 (3) PCT.

2.3 Document D1 is considered to be the closest prior art to the subject-matter of claims 11, 12, 32, 33 and 45 and discloses (see sections 1.1 and 1.2 above) a seed growth method for SWNT where the seeds are prepared by docking metal clusters on the ends of nanotubes by reaction of functionalized nanotubes and metal precursor compounds. The subject-matter of claims 11, 12, 32, 33 and 45 therefore differs from this known D1 in that a specific metal cluster is used. Document D3 discloses the use of FeMoC clusters as active catalysts for the formation of SWNT. However no hint that this type of cluster can be docked on SWNT and that it can be modified by reaction with ethanol is present in the prior art. Therefore the person skilled in the art would not have combined the teachings of documents D1 and D3 when confronted with the problem of choosing an adequate catalyst precursor cluster for the preparation of SWNT seeds. Therefore claims 11, 12, 32, 33 and 45 satisfy the criteria of Article 33 (3) PCT and contain an inventive step..

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/US2004/034002

2.4 Document D1 is considered to be the closest prior art to the subject-matter of claims 57 and discloses a method to obtain SWNTs having at their end metal clusters by functionalizing the nanotubes, reacting them with metal precursors and reducing the SWNT-metal compound complexes in order to obtain carbon nanotube-cluster complexes. The subject-matter of claims 57 therefore differs from this known D1 in that the metal containing compound is functionalized prior to the reaction with the functionalized nanotubes. The effect of this step is a better interaction between the two reactants and a more effective bonding. The problem to be solved may therefore be considered as how to modify the known process of D1 in order to improve the reaction between the precursors and the nanotubes. No hint is given in the prior art to the possibility of performing this intermediate process step therefore claim 57 satisfies the criteria of Article 33 (3) PCT with respect to inventive step.

Re Item VI

Certain documents cited

Certain published documents

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
WO2003/084869	16-10-2003	04-03-2003	04-03-2002

Document D4 (WO2003/084869) discloses the separation of single-walled nanotubes by types and their possible use as seeds.

Re Item VIII

Certain observations on the international application

1 The term "initial attachment" used in claims 13 to 15 is unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claims unclear according to Article 6 PCT.

2 Claims 26 and 27 do not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The claims attempt to define the subject-

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/US2004/034002

matter in terms of the result to be achieved, which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result.

3 The terms "complementary functional groups" used in claims 39, 53, 57 and 59 is unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claims unclear according to Article 6 PCT.

4 It is presently unclear if the "groups that allow for the reaction between the metal-containing compound and the carbon nanotube" of claims 54 and 55 are to be left on the carbon nanotube or on the metal containing compound.